ORGANIC CHEMISTRY

LABORATORY MANUAL
Practical Course

S1 Chemistry Department

Compiled by:

Jamaludin Al Anshori, S.Si.

LABORATORY OF ORGANIC CHEMISTRY
DEPARTMENT OF CHEMISTRY
FACULTY OF MATHEMATICS AND NATURAL SCIENCES
PADJADJARAN UNIVERSITY
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Preface

Organic, chemistry, from its very beginning, has used specific tools and technique for the synthesis, isolation, purification of compounds, and physical method for determination of their properties. Much of the success of the organic chemist depends upon a wise selection and a skillful application these methods.

Technique, and tools, which, with the progress of the science, have become numerous and often intricate In developing material for a laboratory course in organic chemistry, a number of choices must be made, and a course be steered between several conflicting factors. Students very greatly in ability, Schedules are tight for both student time and laboratory space and facility. But the course must not be restricted to a collection of simple cut and dried procedure.

The increasing sophistication of experimental organic chemistry requires more elaborate experiment to provide meaningful and useful experience. This laboratory manual is designed for one semester course in organic chemistry with two four-hour laboratory period per week. The manual is designed to suit the need undergraduate student of chemistry. The authors give the theoretical background for understanding of the operation and a more rational application of the respective procedure. The field is broad and some of it is difficult to survey However, the present laboratory manual didn't cover a comprehensive presentation of technique which used in organic laboratory and which are available for the investigation of organic compounds. Author hope that the manual will be found useful and that many of the readers will let them have benefit or their criticism and of suggestion for improvements.

Compiler,

Jamaludin Al Anshori, S.Si.

KESELAMATAN KERJA DI LABORATORIUM

Keselamatan kerja di laboratorium merupakan hal penting yang harus selalu diperhatikan oleh mahasiswa dan asisten. Semua percobaan kimia sangat berbahaya apabila tidak hati – hati. Lakukanlah percobaan sesuai dengan penuntun percobaan yang telah didiskusikan.

Menangani Kecelakaan

Bila terjadi kecelakaan di laboratorium, beberapa hal yang perlu dilakukan :

1. Semua kecelakaan harus dilaporkan lengkap kepada dosen penanggung jawab praktikum. Bila diperlukan, segera lakukan tindakan dengan memindahkan penderita ke tempat aman dan sesuai dengan tingkat kecelakaan.
2. Harus diketahui dengan jelas tempat dan cara menggunakan alat – alat keselamatan berikut ;
   - Perlindungan / pencuci mata
   - Shower emergency
   - Alat pemadam kebakaran
   - Alat P3K / kotak obat
3. Jika mata terkena zat kimia ;
   - Cuci mata dengan air mengalir segera selama kurang lebih 10 – 15 menit
   - Segera diperiksa ke dokter mata
4. Jika kulit terkena zat kimia ;
   - Cuci kulit dengan menggunakan air sebanyak mungkin, bila perlu gunakan shower.
   - Bila merasa sakit atau iritasi, gunakan obat yang dianjurkan
5. Luka sayat ;
   - Luka sayat kecil, dicuci dengan air dan segera ditutup dengan pembalut luka. Selama bekerja di laboratorium, luka sayat harus tertutup baik.
   - Jika luka sayat cukup parah, stop pendarahan dengan menekan / mengikat dengan kain bersih, segera diperiksa ke dokter.
6. Luka bakar ;
   - Untuk luka bakar yang kecil, simpan air es ke bagian yang terasa sakit. Jangan gunakan apapun di atas bagian yang terbakar, kecuali analgesik setempat.
   - Untuk luka bakar yang lebih parah, segera diperiksa ke dokter.

TATA TERTIB, KEAMANAN DAN KEBERSIHAN LABORATORIUM

1. Praktikan yang berada di laboratorium, tanpa kecuali haruslah mengenakan jas lab termasuk saat - saat kurve dan responsi.
2. Praktikan dilarang kerja di luar jadwal yang telah ditentukan kecuali seijin asisten.
3. Bel tanda masuk dan tanda selesai praktikum harus diperhatikan.
4. Perlengkapan praktikan misalnya ; tas – tas, buku – buku dan lainnya harus ditempatkan ditempatnya dan tidak berada di atas meja praktikan.
5. Pada saat praktikum berjalan, atau pada saat – saat rombongan praktikan berada di dalam laboratorium, semua jendela yang dapat dibuka haruslah terbuka, tanpa kecuali.
6. Absensi dilakukan pada setiap hari kerja dan juga pada jam – jam yang dikehendaki oleh asisten, absensi yang dilakukan di luar jam – jam tersebut haruslah seijin asisten.
7. Praktikan haruslah menandatangani absen yang telah disediakan oleh asisten pada hari – hari kerja atau pun hari – hari atau waktu – waktu yang ditentukan, misalnya ; pada saat – saat pembuatan pereaksi, saat – saat berkumpul untuk mendapatkan tugas – tugas atau pun pengumuman – pengumuman khusus.
8. Setiap ijin meninggalkan jam – jam kerja untuk waktu lebih lama dari 15 menit harus menyerahkan ijin tertulis yang ditandatangani oleh asisten.
9. Sebelum praktikum, praktikan harus sudah benar – benar siap dengan tugasnya, jurnalnya dan segala sesuatu mengenai yang akan dilakukan, termasuk pada saat akan dilakukan pembuatan pereaksi.
10. Jurnal haruslah memenuhi syarat ; terdiri atas nomor percobaan, cara melakukan percobaan (prosedur), sifat – sifat pereaksi dan zat yang akan dihadapi, sifat – sifat reaksi, mekanisme reaksi, teori, referensi dan segala hal yang perlu.
11. Jurnal, tugas, dan laporan haruslah memenuhi ketentuan yang berlaku sesuai dengan yang telah dikemukakan, serta bersih dan rapih. Tugas dan laporan dibuat pada kertas HVS kuarto polos yang pada halaman depannya tercantum kode praktikan, no percobaan, nama, npm, praktikan, tanggal mulai percobaan, tanggal selesai percobaan serta asisten penanggung jawab / asisten mentor praktikan yang bersangkutan.
12. Praktikan yang belum di –ACC jurnalnya tidak dibenarkan kerja (memulai percoban baru).
13. Praktikan yang telah menyelesaikan percoban harus mendapat tandatangan asiten tugas, dan bila telah menyelesaikan semua percobaan yang ditugaskan

diharuskan mendapat tandatangan asisten untuk menyatakan bahwa semua percobaan telah dilakukan sesuai dengan yang ditugaskan.

14. Praktikan yang belum menyerahkan tugas dan laporan untuk melanjutkan praktikum tidak diijinkan untuk bekerja dan dalam hal ini tidak ada penggunaan laporan.
15. Map tugas dan laporan harus senantiasa rapih dan berurut, dan kerapihan serta keteraturannya harus diteliti setiap kurve. Isinya juga harus dari percobaan paling awal di bawah sampai yang baru diatas.
16. Tugas maupun laporan yang telah masuk map tidak bolah diambil kembali oleh praktikan.
17. Praktikan dilarang melakukan kecurangan dalam bentuk apapun yang menyangkut Laboratorium Kimia Organik Jurusan Kimia FMIPA Universitas Padjadjaran, dalam hal ini akan menyebabkan praktikan yang bersangkutan akan dikembalikan ke jurusan masing – masing dan diskor selama 1 atau 2 semester, atau permasalahannya diserahkan ke Universitas.
18. Peringatan yang berulang terhadap kesalahan – kesalahan yang dilakukan akan langsung mempengaruhi nilai praktikan.
19. a. Sebelum praktikum dan pembuatan pereaksi, praktikan harus benar – benar telah siap. Pembuatan pereaksi harus benar – benar efektif dan efisien yang melibatkan seluruh rombongan praktikan, agar tidak menghambat jadwal percobaan yang akan dilakukan untuk setidak – tidaknya 3 sampai 6 paket percobaan yang akan dilakukan, yang dikoordinasikan oleh semua ketua kelompok kerja.

    b. Penggunaan pereaksi – pereaksi PA (GR) dari tempat stock tidak sama sekali dibenarkan, dan pengambilannya pun tidak boleh sembarang, pereaksi jenis PA (GR) haruslah dipindahkan ke tempat pereaksi praktikan terlebih dahulu !!

    Bila ternyata tingkatan PA (GR)-nya telah tidak berlaku lagi karena ulah praktikan, maka tanpa kecuali diwajibkan menggantinya, dan perlu diingat bahwa biaya pembelian pereaksi dengan tingkatan khusus, misalnya PA (GR) jauh lebih mahal dari pereaksi teknis, lebih dari 10 x atau terkadang sampai 50 x harga normal pereaksi non-PA (GR).
20. Semua botol pereaksi haruslah bertanda dan bertanggal, juga berkode.
21. Botol – botol pereaksi, tanpa kecuali haruslah ada tutupnya yang baik dan pas, tutup biasa maupun berpipet.

22. Pereaksi haruslah selalu dalam keadaan teratur dan jelas penamaannya, juga seragam, disertai kode nomor pereaksi, misalnya : 1.1, 1.2, 1.3, dan sebagainya, tertanggal dan selalu dalam keadaan bersih dan rapih penempatannya.
23. Botol pereaksi yang tidak memenuhi syarat tidak sama sekali dibenarkan untuk digunakan.
24. Pereaksi – pereaksi stock harus tetap berada pada ujung meja pereaksi timbangan, yang terdekat dengan meja asisten.
25. Penggunaan pereaksi cair harus menggunakan pipet tetes yang bersih dan tidak berlebihan, pengambilan pereaksi padat harus menggunakan spatula (bukan kertas) dan juga tidak berlebihan. **PERINGATAN KERAS !!!!!!!!!!!!**
26. Kelengkapan yang harus dimiliki oleh praktikan (atau setiap meja) yang harus diambil kembali oleh praktikan pada saat pengembalian meja dan alat – alat praktikum adalah ;
    a. Selang baru untuk pembakar bunsen, dan kondensor – kondensor serta untuk kegunaan – kegunaan lainnya.
    b. Tripleks ukuran 40 x 40 cm. Untuk alas pembakar bunsen.
    c. Balok kayu berbagai ukuran untuk mengatur ketinggian pembakar bunsen serta kegunaan lainnya.
    d. Penunjang kebersihan alat laboratorium seperti halnya sabun, sikat, batu apung dan sebagainya termasuk kain pembersih.
    e. Batu didih yang siap pakai, yang tidak boleh dibuat dalam laboratorium menggunakan alat – alat yang ada di laboratorium.
    f. Kaleng berbagai ukuran untuk pemanas dan kegunaan lainnya. Oli (minyak pelumas bekas) yang bebas air, dan juga pasir (bukan tanah) untuk pemanasan sistem.
    g. Pipet tetes, batang pengaduk, spatula, botol pereaksi dan lain sebagainya.
27. Alat – alat yang ada haruslah digunakan semestinya sesuai dengan kegunaan alat tersebut.
28. Percobaan – percobaan baru dijalankan secara benar, termasuk pemasangan alat, penggunaan alat, kelengkapan serta keamanan sistem.
29. Saat praktikum dilakukan / berlangsung, peralatan maupun perlengkapan yang tidak digunakan tidak dibenarkan untuk berada di atas meja praktikum.
30. Alat – alat yang disimpan dalam laci haruslah selalu dalam keadaan bersih dan siap dipakai. Bila laci atau meja dipergunakan oleh lebih dari satu praktikan, berkomunikasi secara teratur, jujur, efektif sesama pemakai meja, misalnya; melalui surat dalam laci yang mengkomunikasikan mengenai pemecahan alat atau peringatan oleh asisten mengenai alat dan lain sebagainya.

31. Zat – zat kimia tidak samasekali dibenarkan untuk disimpan dalam meja praktikan, kecuali ada ijin tugas secara tertulis.
32. Pengulangan suatu reaksi atau percobaan karena terjadinya kegagalan atau tidak teramatinya hasil reaksi, haruslah seijin asisten tugas, walaupun pada percobaan – percobaan skala tabung reaksi.
33. Pereaksi tanpa kecuali haruslah tetap berada pada meja pereaksi, dan dijaga keteraturannya serta kebersihannya, tidak dibenarkan sama sekali untuk memindahkan pereaksi dari meja pereaksi.
34. Praktikan dilarang merokok dan makan di dalam Laboratorium.
35. Praktikan yang terjadwalkan untuk kurve, diharuskan melakukan kurve tanpa kecuali.
36. a. Pada saat kurve, harus benar – benar diperhatikan bahwa semua daerah lantai, termasuk ruang asisten, ruang gudang, ruang baca, dan ruang praktikan dibersihkan, juga bawah dan sela – sela meja, bak cuci dan sebagainya.
    b. Semua permukaan meja, seperti misalnya : meja praktikan, meja pereaksi, meja timbangan, dan meja baca haruslah dibersihkan.
    c. Pada saat kurve, kursi – kursi yang berada di ruang baca harus dikembalikan ke laboratorium kerja dan ditempatkan di bawah bak – bak cuci, tanpa kecuali statif juga harus ditempatkan kembali ke tempatnya dalam keadaan bersih, rapih, dan teratur.
    d. Praktikan haruslah memperhatikan bahwa timbangan ditutup kembali setelah dibersihkan setiap kali kurve.
37. Sampah – sampah harus dibuang pada tempat yang telah tersedia dan di lantai, bak cuci, laci – laci atau lain sebagainya. Tempat sampah dan daerah sekitar tempat sampah dan daerah sekitar tempat sampah haruslah senantiasa bersih dan rapih.
38. Ruang asam tanpa kecuali haruslah dalam keadaan bersih dan rapih.
39. Praktikan dilarang keras melakukan hal – hal yang dapat membahayakan diri sendiri, yang lain serta keamanan dan ketertiban lab.
40. Praktikan tidak dibenarkan untuk bergurau dengan sesama praktikan selama berada di lab, juga tidak melakukan kegaduhan ataupun mengganggu ketenangan lab.
41. Praktikan dilarang keras melakukan percobaan – percobaan lain yang tidak ada pada penuntun praktikum kecuali seijin asisten dan dalam hal ini termasuk penggantian pereaksi, dan juga cara melakukan percobaan.

42. Meja praktikan, meja pereaksi, dan timbangan, rak pereaksi dan ruang – ruang yang digunakan harus selalu dalam keadaan bersih dan rapih.
43. Bila tidak praktikum tetapi terjadwal untuk kerja, praktikan harus selalu berada di sekitar lab, bila tidak, dapat dinyatakan tidak hadir pada hari tersebut.
44. Praktikan tidak dibenarkan memasuki ruang gudang, ruang asisten, dan laboratorium tingkat sarjana (penelitian) tanpa seijin asisten.
45. Gunakanlah secara efektif ruang laboratorium dan jaga kerapihan dan kebersihannya.
46. Sewaktu meninggalkan laboratorium haruslah selalu diteliti ulang apakah air, gas, listrik, dan jendela telah diamankan.
47. Setiap praktikan yang mengikuti praktikum di Laboratorium Kimia Organik Jurusan Kimia FMIPA Universitas Padjadjaran, tanpa kecuali mematuhi peraturan yang berlaku.

Catatan :

1. Penggunaan zat dan pendukung percobaan lainnya haruslah benar, sesuai dengan tata cara dan dasar pemikiran penggunaan atau pemasangannya.
2. Persyaratan ujian akhir adalah telah menyelesaikan semua masalah mengenai meja dan alat, laporan serta tugas, dan mengumpulkan jurnal praktikum.
3. Alat – alat yang dikembalikan harus dalam keadaan utuh dan bersih, tanpa kecuali.
4. Meja harus dikembalikan dalam keadaan bersih, juga keadaan laboratorium haruslah teratur, bersih dan rapi.
5. Hal – hal lain yang menyangkut tata tertib, keamanan serta kebersihan laboratorium akan diatur kemudian.

LABORATORY TECHNIQUES

This section describes briefly some commonly used laboratory techniques. Not all will be used in this course, but you should be aware of them.

EXTRACTION

In this course, the term "extraction" refers to the process whereby a component in a mixture is transferred into another solvent phase: The operation involves shaking an immiscible pair of liquids, whereby a solute passes from one liquid to the other. Commonly, one of the liquids will be an aqueous (water) solution and the other, an organic solvent (e.g.diethyl ether or CH_2Cl_2) or a solution involving an organic solvent.

Before, using the separating funnel, apply a thin coat of grease or, when dichloromethane is used as solvent, a film of water, to the glass tap (DO NOT grease Teflon taps). Check for leaks by adding a small volume of the solvent to be used to the separating funnel with the tap inserted and closed.

Using the separating funnel:

1. Close the tap.
2. With the separating funnel supported in a ring clamp, add the two liquid phases and insert the stopper.
3. Remove funnel from ring clamp and, holding the stopper firmly with the palm of one hand, invert the funnel and release pressure through the tap.
4. After closing the tap, shake the funnel several times whilst holding both the stopper and the tap.
5. At frequent intervals during an extraction, release excess pressure through the tap. Take care not to point the stem, at your neighbor during this operation.
6. When the extraction is completed, replace the separating funnel in the ring clamp, **remove the stopper** and allow the phases to settle.
7. Drain the lower phase into an appropriate container, and then pour out the upper phase through the neck of the funnel into another container.

RECRYSTALLIZATION

WARNING: DO NOT use a Bunsen burner to heat solutions containing organic solvents.

Recrystallization of a crystalline material is carried out in order to remove impurities. Briefly, the procedure involves dissolving the material in an amount of solvent that will produce a saturated solution at a temperature close to the boiling point of the solvent. Insoluble impurities are removed by gravity filtration of the hot solution and the purified compound crystallizes as the filtrate cools. Suction filtration is used to isolate the purified crystals.

The steps involved in recrystallization may be defined as follows:

1. Select the solvent.
2. Dissolve the material in the hot solvent.
3. Filter the solution if necessary.
4. Allow crystallization to take place.
5. Collect the crystals.
6. Wash the crystals.
7. Dry the crystals. .

The following notes are given to help you to carry out a recrystallization to the best effect.

1 .Selection of a solvent

(a) If the solvent to be used for recrystallization is specified, use that solvent. If the recommended solvent is a mixture of two solvents (for example, ethanol-water), dissolve the material in the more powerful solvent (ethanol for this practical course), filter .the solution if necessary, then add hot water to the hot solution.

(b) If the solvent is not specified, or if several solvents are suggested, it is necessary for you to select a satisfactory solvent. Place a small amount (10-20 mg is sufficient) of the material in a small test tube (the 75 x 10 mm tube is ideal), add two or three drops of the solvent and gently shake

the tube. If the crystals dissolve, that solvent is too powerful -select another solvent for testing. If the crystals do not dissolve, gently warm and shake the tube. If the crystals dissolve, allow the mixture to cool - if crystals do not form, add a **tiny** crystal (a seed crystal) of the material. This is called seeding the solution. If no crystallization occurs, select another solvent; if crystallization occurs, your choice of solvent may be satisfactory. If the crystals do not dissolve on warming, add two or three additional drops of solvent and continue warming. Repeat the addition of solvent until a total of about 0.5 ml (10 mm in the 75x10 test tube) of solvent has been added. If the crystals still do not dissolve, select another solvent.

NOTES:

(i) Large crystals of some compounds dissolve very slowly even in solvents in which the compound has a high solubility: if the crystals are large, use a glass rod to crush them in the test tube before testing for solubility.

(ii) If your first choice of solvent is unsatisfactory, you must use a fresh portion of the material to be recrystallized for testing the next solvent.

(iii) If the crystals dissolved in the hot solvent but recrystallization did not occur on cooling the mixture, it may be satisfactory to reduce the solubility of the required compound by the addition of another solvent, completely miscible with the first solvent and in which the required compound has a very low solubility. This procedure is commonly called "using a mixed solvent" The second solvent is added drop wise to the hot solution until a cloudiness appears. At this point, warm the mixture to give a clear solution or add a very small amount of the first solvent (to give a clear solution), seed the solution and allow it to cool.

Having selected the solvent for recrystallization, the next step is -

2. Preparation of the solution

Retain, for seeding, a tiny sample of the material that is to be recrystallized and transfer the remainder into a conical flask.

Add some of the selected solvent and a few boiling chips and heat the mixture to boiling. Add more solvent in small portions, reheating the mixture to boiling after each addition, until a clear solution, apart from insoluble impurities, is obtained. Now add more solvent, approximately 1/10th of the volume of the solution, and reheat: The mixture is now ready to be filtered (but see NOTE (ii)).

NOTES:

(i) If some of the material to be recrystallized does not dissolve after more solvent has been added, rather than continue to add solvent, decant the solution carefully into another conical flask, leaving the bulk of the insoluble material in the first flask. Add a portion of solvent to the first flask and heat the mixture. It will soon become apparent if the solid begins to dissolve. If the solid does not dissolve, it is reasonable to treat this as an impurity. If the solid dissolves, combine the two solutions.

(ii) Use of decolorizing charcoal the crude product of an organic reaction may contain a colored impurity. During recrystallization, this impurity may dissolve in the boiling solvent and be partly absorbed by the crystals as they separate upon cooling, yielding a colored product. Sometimes the solution is slightly turbid owing to the presence of a little resinous matter or a very fine suspension of an insoluble impurity, which cannot always be removed by simple filtration. These impurities can be removed by boiling the solution with a little decolorizing charcoal for 2-3 minutes, and then filtering the solution while hot. The decolorizing charcoal adsorbs the colored impurity and holds back resinous, finely-divided matter, giving a filtrate that is usually free from extraneous color, and therefore capable of depositing pure crystals. An excessive quantity of decolorizing agent must be avoided, since it may also adsorb some of the compound which is being purified. The exact quantity to be added will depend upon the amount of impurities present; for most purposes 1-2 percent by weight of the crude solid will be found satisfactory. If this quantity is insufficient, the operation should be repeated with a further 1-2 percent of fresh decolorizing charcoal. Sometimes a little charcoal passes through the close-grained filter paper: the addition, before filtration, of filter aid, a

diatomaceous earth, will give a clear filtrate. Alternatively, the hot solution may be filtered through a pad of filter aid. Attention is directed to the fact that the decolorizing charcoal (or any, other powdered solid) should not be added to a superheated solution as the latter may foam excessively and boil over. Therefore, dissolve the crude product in the minimum amount of boiling solvent and allow the solution to cool a little before adding the charcoal and filter aid. Add fresh boiling chips immediately before reheating.

3. Filtering the hot solution

Filter the hot solution through a **small** plug of filter wool, or a **fluted** filter paper (if charcoal is used), supported in a preheated, short-stemmed conical funnel.
The funnel is supported in a conical flask which is large enough to hold all of the solution. If any material crystallizes in the filter assembly, it may be scraped back into the first flask, redissolved, and the solution filtered as before.

4. Crystallization

Allow the hot filtered solution to cool slowly to room temperature. If crystallization does not start soon after the hot filtration, add a very small crystal from the sample set aside for the purpose. This addition of a seed crystal is the most satisfactory procedure for inducing crystallization. If the seed crystal dissolves, wait for a few minutes, during which time the solution will cool further, then add another seed crystal.
After the solution has cooled to room temperature, cool the mixture in cold water (about 10 ^{O}C is cold enough) for a few minutes in order to ensure that the crystallization is complete.

5,6. Collecting and washing the crystals

If the crystals adhere to the walls of .the flask, scrape them loose using a spatula, then collect the crystals in a **Buchner** funnel (for a large amount) or in a **Hirsch** funnel (for a small amount) using vacuum filtration.

Before attempting to collect the crystals moisten the filter paper with the solvent used for recrystallization and press it down on the perforated disc in order to "seal" it to the funnel. Apply suction to the filter flask or tube, swirl the crystal and solution and pour the mixture into the .funnel. If crystals remain in the flask, they may be transferred to the filter by use of a spatula, or by adding a small amount of the recrystallization solvent, or some of the filtrate, to the flask, swirling the crystals and liquid as before, then quickly pouring the mixture into the funnel. As soon as filtrate ceases to flow from the bottom of the funnel, disconnect the vacuum hose from the flask. Now add enough cold recrystallization solvent to just cover the crystals in the funnel, rinsing the sides of the funnel at, the same time. Reconnect the vacuum hose and remove as much solvent as possible by suction. This washing step is important. It removes solution (containing soluble impurities) that coats the crystals.

NOTES:

(i) Successful purification by recrystallization requires complete removal of solution from the crystals. After air of the crystals have been transferred to the funnel and most of the solvent removed by suction, it is often useful, especially when large amounts are being handled in the Buchner funnel, to press down the crystals using a small conical flask or a 2 x 1 sample tube. This produces a firm pad of crystals from which the mother liquor (the name given to the liquid phase after crystallization from a solution has taken place) is more readily removed.

(ii) It is important to avoid drawing air through the pad of crystals before the crystals have been washed with fresh solvent as deposition of soluble impurities on the surfaces of the required crystals may occur.

7. Drying the Crystals

If an organic solvent (other than methanol or ethanol) has been used for the recrystallization, it is usually sufficient to allow the traces of solvent surrounding the crystals to evaporate by spreading the crystals out on a piece of paper or a watch glass for a few minutes.

If an aqueous solution has been used, the crystals should be dried under reduced pressure by placing them in the vacuum desiccator over the silica gel desiccant. This gel is impregnated with a cobalt salt which is bright blue when the gel is dry and pale pink when it is saturated with water. Ensure that the gel which you use is dry. Pink gel can be returned to the service room for recycling.

Keep the desiccator lid on **at all times** unless actually placing material in or taking it out!

Steam Distillation

This procedure provides a simple method for the isolation from an aqueous mixture for a mixture of two immiscible liquids, the total vapor pressure is the sum of the separate vapor pressures of the two components, and independent of the relative amounts (that is, Raoult's law does not apply to this system). As the mixture will distil when the total vapor pressure is equal to the atmospheric pressure, the boiling point of the point of the mixture will be lower than that of either constituent. Thus, for example, aniline can be removed from a reaction mixture by passing steam into the mixture. Water and aniline distill from the mixture at approximately 98.6°C (at this temperature, the vapor pressure of pure water is 723 torr and the vapor pressure of aniline is 38 torr).

Note that during steam distillation the volume of liquid in the distillation flask increases (due to condensation of steam); therefore try to keep the initial volume as low as possible by using only small amounts of water to rinse out the reaction flask, and by stopping the steam distillation as soon as the removal of product is complete.

Use of Rotary Evaporators

Rotary evaporators are used for removing the solvent at reduced pressure (and therefore at lower temperature than its "normal" boiling point) and without using boiling chips.

Bath temperature should not exceed the "normal" b.p. of the solvent. For common organic solvents 35-40 ^{0}C is sufficient; for aqueous solutions the temperature may be somewhat higher. The Quick fit RB flask should not be more than half full.

To start:

1. Check the bath temperature.
2. Turn on cooling water.
3. Turn on water pump -fully.
4. Attach distillation flask.
5. While still supporting the distillation flask, close the tap on condenser to start vacuum.
6. Immediately start rotation.
7. Once the vacuum is holding the distillation flask, remove the supporting hand.
8. Depress the button on the handle and lower the distillation flask into the bath. (Note: older machines have a handle which must be turned anticlockwise before the flask can be raised or lowered. When in position the flask is arrested by SLIGHTLY turning the handle clockwise. Use of excessive force will ruin the mechanism.)

To Stop:

1. Lift the distillation flask from the bath
2. Stop the rotation.
3. Release the vacuum and remove the distillation flask.
4. Turn off the pump and cooling water.

THIN–LAYER CHROMATOGRAPHY

This is a reliable and quick method for determining the extent of contamination of products by impurities of significantly different polarity. The method can be used routinely to check the purity of non-volatile materials.

Procedure:

1. Slurry of silica gel in chloroform (centre or side bench) is stirred with the stout rod provided to ensure an even consistency.

2. Two clean microscope slides are placed face to face, dipped into the slurry and returned quickly to a horizontal position so that the coating of gel remains even.
3. The slides are separated carefully, waved gently to allow the evaporation of the chloroform, and allowed to dry, gel side up, for a few minutes.
4. A small volume of developing solvent (Chloroform is especially effective but other solvents may be tried) is poured into a chromatography jar (service room) to a depth of no more than 3 mm and the plastic cap is replaced.
5. A section of soda-glass tubing is heated to **extreme softness using a Meker burner** (side benches). The grass tubing is then removed from the flame and immediately pulled out steadily into a long length of fine-walled capillary tubing. This is cut, using an emery block, into lengths of ca. 8 cm.
6. A very small quantity (< 1 mg) of the material to be analyzed is placed in a small sample tube and dissolved in a **spotting solvent** (1 drop). Dichloromethane is usually effective as the solvent.
7. A length of the cut capillary is used to transfer spots of the solution to be analyzed, to a site on the microscope slides silica surface ca. 8 mm from the fully-coated end. Gentle waving removes the solvent. Spotting can be continued at a site to enhance the response in the detection stage (below). As many as four sites can be spotted across a single slide.
8. The microscope slide is placed, spotted end down, in the solvent in the chromatography jar and the cap is replaced. The solvent climbs up the gel coating and chromatographic separation may occur. Note that no part of a sample spot must be immersed in the solvent.
9. When the solvent front has almost reached the top of the silica gel, the slide is removed from the jar and the position of the solvent front is marked quickly using a pointed instrument. The slide is then allowed to dry.
10. The colorless spots are detected on the dry plate using an iodine vapor jar or, in certain cases, a UV lamp. The identifying feature of a material is the Rf, the distance traveled by the spot divided by the distance traveled by the solvent front, both measured from the centre of the starting spot.

EXPERIMENT 1: CROSSED ALDOL CONDENSATION BETWEEN ACETONE & BENZALDEHYDE

For General Science students only. *This* experiment is slightly less demanding than Experiment 3A, but it will provide experience with one of the reactions learned in the carbonyl chemistry sections of the lecture course and will allow students to demonstrate their skill in preparing a crystalline compound in pure form.

The aldol reaction (literally: ***ald****ehyde-alcoh****ol*** forming) is one of the most fundamentally *important* carbon-carbon bond forming processes available to synthetic organic chemists. It is the parent of a family of reactions of carbonyl compounds and is a favourite reaction of Nature. It can be promoted by acids or bases. In this experiment, a base-catalyzed, two-fold crossed aldol reaction will be performed, but the intermediate aldol product will undergo loss of water, in a secondary Schmidt dehydration reaction, to give an α,β-unsaturated carbonyl compound, dibenzalacetone.

With the aid of your textbook, devise a mechanism for the reaction and explain why it is called a crossed-aldol reaction.

$$PhCHO + CH_3COCH_3 \xrightarrow[EtOH]{NaOH} PhCH{=}CHCOCH{=}CHPh$$

EXPERIMENTAL

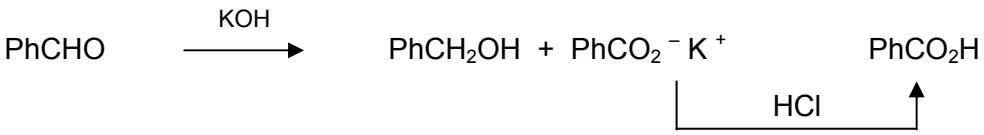
Dissolve sodium hydroxide pellets (2.5 g) in water (25 ml) in a 100 mL conical flask, and after solution is complete, add 95% ethanol (20 mL) to the mixture, swirl the flask and allow the contents to cool to room temperature.

Prepare a mixture of freshly distilled benzaldehyde (2.7 g) and acetone (0.8 g; approximately 1 mL) and add this drop wise, with shaking, *via* a Pasteur pipette into the alcoholic hydroxide solution. The addition should take about 5 minutes. Allow the mixture to stand for a total of 30 minutes with occasional shaking; a precipitate begins to form after about 10 minutes. Collect the product under suction on a large Hirsch funnels (see Techniques), wash it well with water to remove excess alkali, and recrystallize the solid from ethanol (see Techniques).

Record the yield and melting point of the product, that in the literature.

EXPERIMENT 2: CANNIZARO REACTION OF BENZALDEHYDE

This experiment is closely related to the aldol reaction, which was described in Experiment 1, but yields two products that will be chemically separated and individually isolated and purified. It is an example of an oxidation/reduction process that occurs only with aldehydes that have no protons on the carbon next to the carbonyl group. Outline a mechanism for the reaction in your report.



EXPERIMENTAL

Dissolve potassium hydroxide pellets (14 g) in water (13 mL) in a 250 ml conical flask. *(CAUTION:* Concentrated alkali is highly corrosive. Should it be spilled on your skin, wash the affected area immediately with copious quantities of water. The reaction mixture wiII become hot). Cool the mixture to room temperature then add freshly distilled benzaldehyde (15 g). Stopper the flask securely, and shake it well to generate a thick emulsion. *(Note:* Unless an emulsion is formed, the reaction will not proceed. If necessary, continue shaking the flask,) Set the emulsion aside in your locker for one week. At this stage Experiment 3 can be commenced.

ISOLATION OF THE PRODUCTS

Reminder: You are required to isolate **two products** from this reaction. Follow the instructions carefully be aware that the compounds will be separated into different phases, .and do not discard layers until you are sure that you have isolated the desired substances.

Dilute the mixture with water (ca. 55 ml) and swirl the flask until all of the crystalline potassium salt has dissolved. Transfer the mixture to a separatory funnel and extract the solution with dichloromethane (lower layer) (25 mL). Extract the upper aqueous layer twice more with fresh portions of dichloromethane (2 x 20 ml) and combine the organic layers. **Retain both aqueous and dichloromethane layers in separate flasks.**

ISOLATION OF BENZYL ALCOHOL

Note: The following procedure relies upon formation of a water-soluble bisulfite complex (RCHO. HSO_3^-) to remove unreacted benzaldehyde from the benzyl alcohol.

Return the combined dichloromethane layers to the separatory funnel. *(CAUTION:* Pay particular attention to retain the desired organic layer. DO NOT discard washing .layers until you are sure you have the product.) Extract the solution in, turn with saturated aqueous sodium metabisulfite (normally the lower layer) (1 x 10 mL, then 1 x 5 mL), saturated aqueous sodium carbonate (upper layer) (1 x 10 mL) and water (upper layer) (1 x 10, mL). Dry the organic phase over sodium sulfate, filter the solution and remove the solvent on a rotary evaporator.

Distill the residual benzyl alcohol and **record the boiling point range, yield and refractive index of the product.**

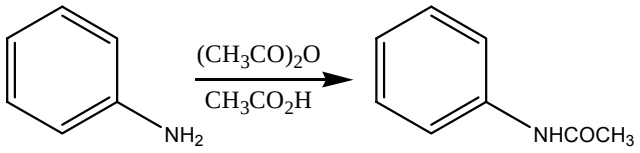
ISOLATION OF BENZOIC ACID

Add the original aqueous layer to a freshly prepared mixture of ice (50 g), 10M hydrochloric acid (40 mL) and water (40 mL). Collect the precipitated benzoic acid in a A Buchner funnel under suction. Recrystallize the crude product from water in a 250 mL conical flask *(CAUTION:* Benzoic acid is steam volatile. You will need about 200 mL of water, but DO NOT use too much, Place a watch glass over the recrystallization flask to avoid losses in the steam.) Dry the product thoroughly in a desiccatar. **Record its yield and melting point.**

Compare the physical constants for the two products with values from the literature.

EXPERIMENT 3: PREPARATION OF ACETANILIDE

In this experiment you encounter the acetylation procedure which is effective in characterizing and identifying hydroxy and amino compounds and serves to protect sensitive materials from oxidation. Provide a mechanism for the reaction.



EXPERIMENTAL

ACETYLATION OF ANILINE

CAUTION: Aniline; like many other aromatic amines is toxic by both inhalation and absorption through the skin. Take appropriate precautions. Handle it in the *fume* cupboard. Should it be split upon you, wash it off **immediately** using ethanol and without rubbing, then wash well using water.

Dissolve aniline (7.0 g) in glacial acetic acid. (17 M; 7 mL) in a 50 ml Quickfit flask. Swirl the flask to ensure thorough mixing. Add acetic anhydride (9 mL), immediately attach a reflux condensor and heat the solution at reflux *for* 10 min (fume cupboard). Pour the hot liquid in a thin stream, with constant stirring, into a beaker containing water and ice *(ca.* 60, ml). Filter off the crude product using the Buchner assembly .

PURIFICATION OF ACETANILIDE

Crystallize the crude acetanilide from water (ca. 150 mL), filtering the hot solution through filter wool in a preheated funnel. Collect the crystal in the cleaned Buchner apparatus and transfer this product to the bottom part of a **preweighed** Petri dish with cover. Dry the acetanilide **to constant weight** using a desicant in the vacuum desicator. This process will probably take 2 weeks and require you to renew the desicant in your desicator after one week.

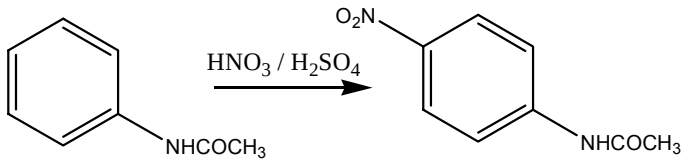
Do not proceed to the next synthetic step using wet acetanilide. Experiment 4 : Preparation of *p*-nitroacetanilide should be commenced only at the beginning

of a laboratory session and be performed using acetanilide with m.p > 110^{o}C. whilst the sample is being dried, continue work on the unknowns or on Experiment 4.

Determine the yield and m.p. of the pure acetanilide. The material which is not used in experiment 4 **should be submitted with your report.**

EXPERIMENT 4: PREPARATION OF *p*-NITROACETANILIDE

This experiment demonstrates the directing ability of the acetamido group in electrophilic aromatic substitution. In the introduction to your report, provide a mechanism that clearly shows this directing effect.



EXPERIMENTAL

THE AROMATIC NITRATION

Dry acetanilide (m.p. > 11O °C; 5.2 g) is dissolved in acetic acid (17M; 6.0 ml) with warming in a 50 mL conical flask. The temperature of the solution is measured and sulfuric acid (18M; 10 mL) is added in small portions with shaking whilst cooling the solution in ice to keep the temperature below 40°C, This mixture is cooled to below 5°C and "nitrating acid" (fume cupboard; 5.0 ml) is added dropwise, with shaking in the ice bath, **at such a rate that the temperature does not reach 10°C. This is must important and may take up to 20 min.**

When the addition is complete, the solution is left in the ice bath for 30 min and then poured into ice-cold water (100 - 150 mL). The precipitate is allowed to stand for 10 min, collected by suction filtration, pressed to expel the aqueous phase and washed with water (100-200 ml); .The product should be very pale yellow, (Colour is due to the presence of the orange-yellow *o*-isomer.)

PURIFICATION OF *P*-NITROACETANILIDE

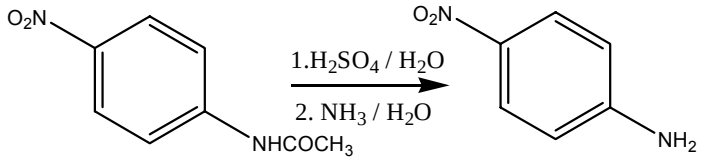
The crude product is crystallized from 95% ethanol (about 70 ml). (Note: You should reach this stage before the end of the laboratory session.) The pure product crystallization and separation is completed by cooling throughly in ice. Collect the crystals by suction filtration.

Dry the product, record the yield of the pure product. together with its m.p. Compare the latter with.a literature value. If the product is sufficiently pure, proceed to Experiment 5 and submit the remainder with your report.

***Nitrating acid is kept in the fume-hood** and is prepared by mixing conc. nitric acid (55 mL) with conc. sulfuric acid (35 ml).

E X P E R I M E N T 5 : PREPARATION OF *p*-NITROANILINE

This experiment demonstrates the acidic hydrolysis of amides. Compare the mechanism with that involved in Experiment 5.



EXPERIMENTAL

HYDROLYSIS OF *p*-NITROACETANILIDE

A mixture of *p*-nitroacetanilide (3.0 g) and 70% sulfuric acid* (16 mL) is warmed to dissolve the solid and the solution heated at reflux in a 50 mL Quickfit flask for 30 min.

The solution is poured into water (100 mL), the mixture is cooled and made alkaline using 15M aqueous ammonia. **When this mixture is old**, the solid product is collected by suction filtration, washed with Water and then crystallized from ethanol-water *(ca.* 1:1).
Record the yield of the pure product and compare its m.p. with the literature value.

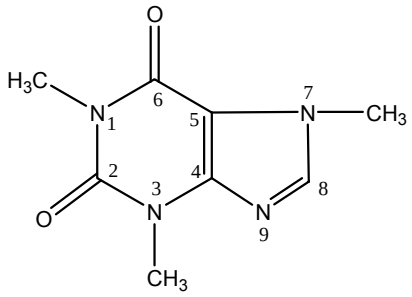
*This reagent is kept on the centre reagent rack and is prepared by the careful dilution of 18M sulfuric acid (40 mL) with water (30 mL).

ISOLATION ORGANIC COMPOUND FROM PLANT

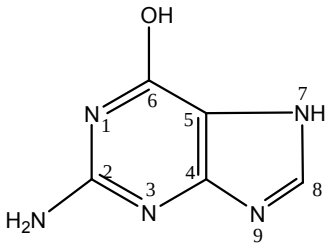
1. Introduction

The stimulating effect of aqueous infusions *of* coffee beans, tea and mate leaves, and cola ,nuts is due mainly to the presence of caffeine, a nitrogen heterocycle of molecular formula products and synthesis to be 1,3,7 -trimethyl -2,6-dioxopurine. Tea leaves contain 3--5 percent of caffeine and a trace of theophyline, a lower homologue lacking the methyl group at position 7.

These compounds are related structurally to the important purynes, adenine and guanidine, that are present.in RNA and DNA.



Caffeine



Guanine

Structure of caffeine and Guanine

In this experiment the caffeine is extracted from tea leaves by hot water, in which it is quite soluble (about 18g / 100 ml at 80 ^{0}C; 2.2 g/100 ml. at 20 ^{0}C). Colored impurities such as tannin acid can be removed as calcium salts by addition of calcium carbonate. From the aqueous extract the caffeine is isolated conveniently by multiply extaction small portions of chloroform (or dichloromethane), in which caffeine is very soluble. Caffeine forms a monohydrate that loses water rapidly on warming to give the anhydrous form, m.p. 238 ^{0}C.

2. Procedure

In a 500 ml, Erlenmeyer flask place 30 g of ordinary dry tea, 300 ml of water, and 15 g. of powdered calcium carbonate. After boiling the mixture gently with occasional swirling for 20 minutes, filter the hot mixture on a Buchner funnel and press the filter cake firmly with a large cork to obtain as much as possible of the liquid.

Cool the aqueous extract to 15 - 20 ^{o}C, transfer it to a separatory funnel, and extract the caffeine with three successive 25 ml. portions of chloroform or dichloromethane. Pour the combine chloroform extracts into an Erlenmeyer flask and add 0.5 g. sodium sulfate Decant the chloroform solution from sodium sulfate in decant flask. Add a broken wood splint or a boiling chip to the solution to prevent violent bumping and evaporate the solvent on steam bath. Scrape the dry product from the flask and weigh the crude caffeine.

Dissolve the crude in minimum amount (+ 4 ml.) of boiling benzene. Filter the hot solvent in and allow it to cool slowly in a cork flask. After crystallization has occurred, cool the flask in ice. Collect the crystals in a Buchner funnel, dry in air and weigh. A second batch of caffeine can be obtained by heating the filtrate to boiling and adding petroleum ether (90 - 100 ^{o}C) at the boiling point until cloudiness appears. Add just enough hot benzene to clear up the cloudiness and set the solution a side to cool. Calculate the present of total recovery based on the amount of crude caffeine.

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